

Materials Science and Technology

Nanoscience

Solution-Templated Nano-Architectures for Ultracapacitors

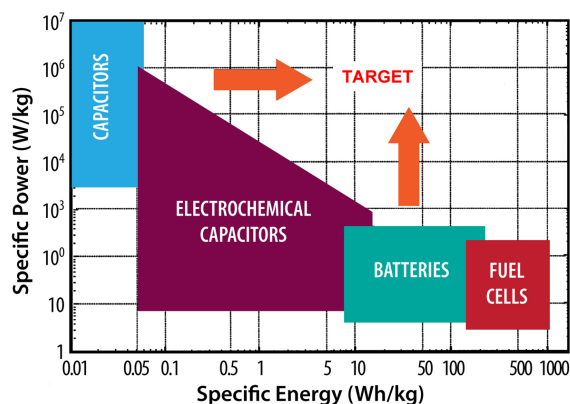


Figure 1: A Ragone plot showing energy and power characteristics of energy storage devices and future target.

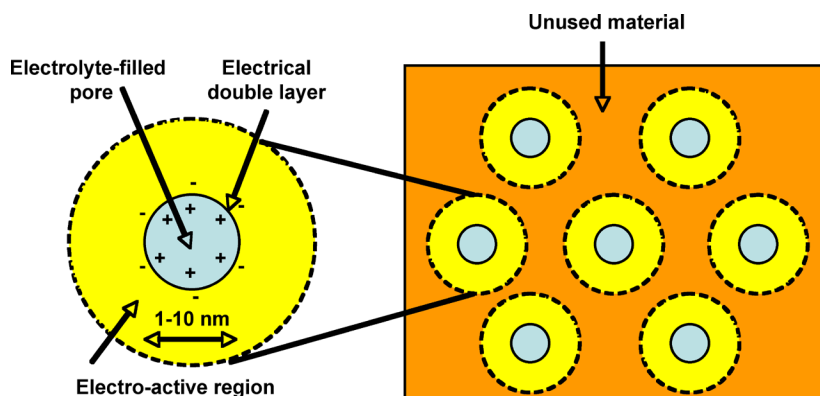


Figure 2: A schematic showing how ultracapacitors work. Electrons and counter-ions flow into and out of electroactive materials from the electrolyte. Maximum performance is achieved when all material is sufficiently close to electrolyte interfaces to be accessed.

Materials utilizing both electrochemically-active oxides and conductive polymers are promising candidates for increasing energy storage

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Electrical energy storage is becoming increasingly important to a broad spectrum of critical technologies, ranging from the electrical power grid and electric vehicles to microsystems for both commercial and defense applications. In all of these applications, the drive is to increase both energy densities (related to the charge stored per unit volume), and power densities (related to how rapidly the charge can be stored and released), as depicted in Figure 1. Ultracapacitors are unique electrical energy storage devices that can simultaneously achieve the high energy densities associated with batteries and the high switching speeds and power densities associated with capacitors within a single material. By using simple and inexpensive solution-based processing methods, Sandia researchers are now exploring ways to maximize ultracapacitor performance by producing nano-architectures utilizing both electrochemically-active oxides and conductive polymers.

To achieve the highest levels of performance, materials in ultracapacitors must be: 1) electrochemically active (capable of being oxidized and reduced under an applied voltage), 2) capable of conducting both electrons and charge-compensating counter-ions (such as protons or sodium ions), and 3) organized within a high surface area architecture to maximize contact with electrolyte solutions and minimize transport distances for electrons and ions. These ideas are shown schematically in Figure 2. Sandia is exploring a wide range of solution-based schemes in which structural elements that are of nanometer dimensions (tens of atoms thick) are used as templates for the growth of electroactive materials (Figure 3). In some instances, arrays of organic surfactants serve as templates for creating nano-architectures in electroactive oxides, while in other instances, high surface area oxides are used as templates for the polymerization of conductive polymers. In mixtures containing both active oxides and conductive polymers,

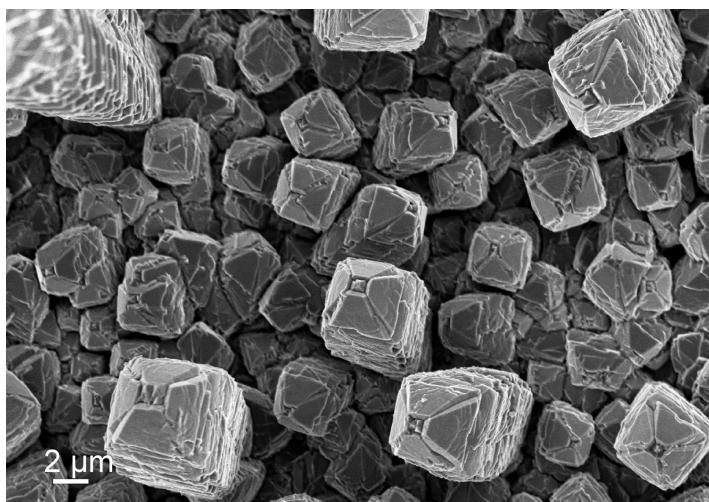


Figure 3: An electron micrograph of hydrothermal MnTiO_x grown at Sandia. Here, clay-like nano-layers within each pillar provide electrolyte access rather than pores.

each material in the nanostructure can contribute to the overall performance. One element may provide conductive pathways for electrons, while another material provides conductive pathways for ions.

A specific example showing the benefits of solution-prepared nanostructures is provided by the use of surfactants to organize the formation of electrochemically active

ruthenium oxide (Fig. 4). Sulfur groups in the surfactants bond to the dissolved ruthenium species used to produce thin films via spin coating. The surfactant sterically blocks sites that would normally be available for the formation of an extended oxide. On heating, the surfactant decomposes, leaving behind a structure consisting of interconnected molecular clusters having sub-nanometer dimensions. Electrochemical measurements show that this structure has over three times the capacitance and power density of bulk ruthenium oxide. This is because: 1) all ruthenium atoms are within a few atomic dimensions of the electrolyte solution, minimizing transport distances, and 2) the clusters retain high hydroxyl group concentrations, providing for enhanced proton conductivity. Work is now progressing to systems containing conductive polymers with redox potentials, energy densities, and power densities that can be selectively tuned to match a broad range of energy storage applications. Early results indicate that it should be possible to achieve performance enhancements using materials that are substantially cheaper and easier to make than ruthenium oxide. Sandia is also starting to explore how similar templated techniques could be used to create nano-architectures that are optimized for anodes, cathodes, and separators for batteries and other energy storage systems.

Figure 4: (Top) - Ruthenium-surfactant complexes (left) react with each other to form interconnected molecular clusters of ruthenium oxide. (Bottom) - Electron micrographs show that the resulting films exhibit hierarchical porosity to optimize electrolyte access and minimize transport distances. Large pores are bubbles forms via template decomposition, while small pores are defined by the molecular clusters of RuO_2 .

